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POSITIVE AND NEGATIVE CHARACTER OF CHLORINE AND NITROGEN IN THEIR COMPOUNDS.

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THE POSITIVE AND NEGATIVE CHARACTER OF CHLORINE AND NITROGEN IN THEIR COMPOUNDS

BY

ARTHUR BLAINE HAW

B. S. Harvard University, 1913.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY ARTHUR BLAINE HAW

ENTITLED POSITIVE AND NEGATIVE CHARACTER OF THE HALOGENS IN COMBINATION WITH NITROGEN

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

W. A. Noyes
In Charge of Thesis

W. A. Noyes.
Head of Department

Recommendation concurred in*

Committee on Final Examination*

*Required for doctor's degree but not for master's

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During recent years the structure and characteristics of the atom have been given much thought by chemists. Arrhenius[1] proposed the hypothesis that electrolytes separate in various degrees in aqueous solution into electrically charged ions, which may combine with other ions present in the same solution, or recombine on evaporation of the solution. This hypothesis has been generally accepted, and has led to much speculation as to the part played by electrical forces in the atom.

Ostwald[2] applied a similar principle in discussing the formation of ozone by the action of oxygen on phosphorus. In the paper by Noyes and Lyons[3], in discussing the reaction of chlorine and ammonia, the suggestion is made that the chlorine molecule may separate into positive and negative ions Cl^- and Cl^+, and that some of the nitrogen and hydrogen atoms were temporarily positive and others were negative while reacting.

Similar ideas had been used by Stieglitz[4] in his classroom for several years in explaining such reactions as that of chlorine and water.

$$Cl^- + Cl^+ + H^+ + OH^- = HCl + ClOH$$

Later an hypothesis was proposed by J. J. Thompson[5], relating electrical forces within the atom and valence, in which electrons, or atoms of electricity, are assumed to be present and their transfer may be the cause of chemical combination. Further developments along this

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1 Z. Physik. Chem. 1
2 J. Am. Chem. Soc. 23, 463 (1901)
3 J. Am. Chem. Soc. 23, 460 (1901)
4 J. Am. Chem. Soc. 23, 797 (1901)
5 Phil. Mag., March 1904

line have been offered by Abegg[1], Falk and Nelson[2], and Fry[3], in which the electron theory of valence is elaborated and applied particularly by the last three authors to organic compounds.

In 1900 Chattaway and Arton[4] found that when nitrogen iodide reacts with any reducing agent, according to the following reaction

$$N_2H_3I_3 + 3H_2O + R = 2NH_4I + HI + R(O_3)$$

the ratio between the amount of reducing agent oxydized and that of the hydriodic acid produced is as 2 : 1, and that the iodine in the nitrogen iodide behaves in these reactions as the chlorine contained in a hypochlorite and exerts twice its normal oxidizing power. That the chlorine in nitrogen trichloride is equivalent to six atoms of available chlorine was first pointed out by Seliwanow[5], and was later confirmed by Hentschel[6] and Noyes and Lyons[7]. This indicated that the nitrogen in these compounds is negative and the halogen positive, and the nitrogen trichloride would hydrolyze as follows.

$$N^{---}\ Cl_3^{+++} + 3H\ O^{--}\ H^{+} = N^{---}\ H_3^{+++} + 3Cl^{+}O^{--}\ H^{+}$$

Assuming that the charges on the atoms of the nitrogen trichloride are reversed, we should have another compound which Noyes calls nitro nitrogen trichloride, the ordinary form being called ammono nitrogen trichloride, and which would hydrolyze as follows.

$$N^{+++}Cl_3^{---} + 3H^{+}OH^{*} = H^{+}O^{--}\ N^{+++}O^{--} + H^{+}\ O^{--}\ H^{+} + 3H^{+}Cl^{-}$$

The present investigation was undertaken to try and prepare this

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1 Z. Anorg. Chem. 39, 342 (1903)
2 School of Mines Quart. 30, 179 (1909); J. A. C. S. 33, 1140 (1911)
3 Z. Physik. Chem. 76, 385, 398, 591 (1911)
4 Am. Chem. J. 24, 138-167 (1900)
5 Ber. 27, 1012 (1894)
6 Ber. 30, 1434 (1897)
7 J. Am. Chem. Soc. 23, 460 (1913)

nitro nitrogen trichloride. The isolation of such a compound would give support to the hypothesis that electrical charges exist in compounds as well as being formed during ionization of compounds in solution, and would support, also, the electron conception of valence.

EXPERIMENTAL

Experiments With S_2Cl_2

The first reactions were carried out with compounds in which the nitrogen of one compound was positive and the chlorine of another compound was negative, with the idea in mind that a union would take place between the positive nitrogen and the negative chlorine. The compound selected to yield the nitrogen was nitrosyl chloride. Nitrosyl chloride hydrolyzes normally to nitrous and hydrochloric acids, and its nitrogen is clearly positive. Compounds selected to yield negative chlorine were the chlorides of phosphorus and sulfur. Nitrosyl chloride (NOCl) was prepared by passing a slow stream of dry nitric oxide through liquid chlorine, kept cold with solid carbon dioxide and alcohol. This product always contained an excess of free chlorine. It was collected by passing the gases into a small bulb, cooled by means of solid carbon dioxide and alcohol contained in a Dewar bulb, any excess being sealed up for future use. The experiment was carried out in the apparatus shown in Figure 1.

The NOCl from one of these bulbs was allowed to evaporate slowly through some S_2Cl_2, contained in a glass stoppered wash bottle surrounded by water which was kept at 60°, thus driving any of the products of the reaction over into the long tube connected with the wash bottle, which was surrounded by a freezing mixture of ice and

commercial hydrochloric acid. Connected with the tube was a series of four U tubes sealed together. The first U tube was surrounded by solid CO_2 and alcohol, contained in a Dewar bulb, and by this means any of the products which did not condense in the long tube would be condensed here. When all the NOCl had evaporated, the freezing mixture was removed from the long tube and it was allowed to warm up to room temperature, the products being condensed in the U tube. Finally the material that had condensed in the U tube was fractionated from one U tube into the next, the final product being distilled into a small bulb, cooled with solid carbon dioxide and alcohol, and sealed up until ready for analysis.

Method of Analysis. The analysis was carried out by allowing the condensed gases to evaporate through a weighed bulb, which was eventually filled with the gas. It was then sealed and reweighed and opened with the tip immersed in an N/10 standard potassium hydroxide solution, which was drawn in as the gases were absorbed. The bulb was then reweighed with the solution. The solution was then made up to 100 cc. and analyzed for chlorine, acid, reducing power, sulphur and nitrogen. The volume of the bulb was determined by weighing it filled with air and distilled water.

			Mols	Cl	Acid	Weight
Mols of gas	2.62	NOCl	2.51	2.51	5.02	0.1644
Mols of acid	5.34	SCl_2	0.07	0.14	0.21	0.0072
Atoms of Cl	2.69	Cl_2	0.05	0.10	0.10	0.0035
			2.63	2.75	5.33	0.1751
Atoms of O	2.18					
Atoms of S	0.07	Found	2.62	2.69	5.34	0.1765
Atoms of N	2.51					

The results show no evidence of the nitrogen trichloride having been

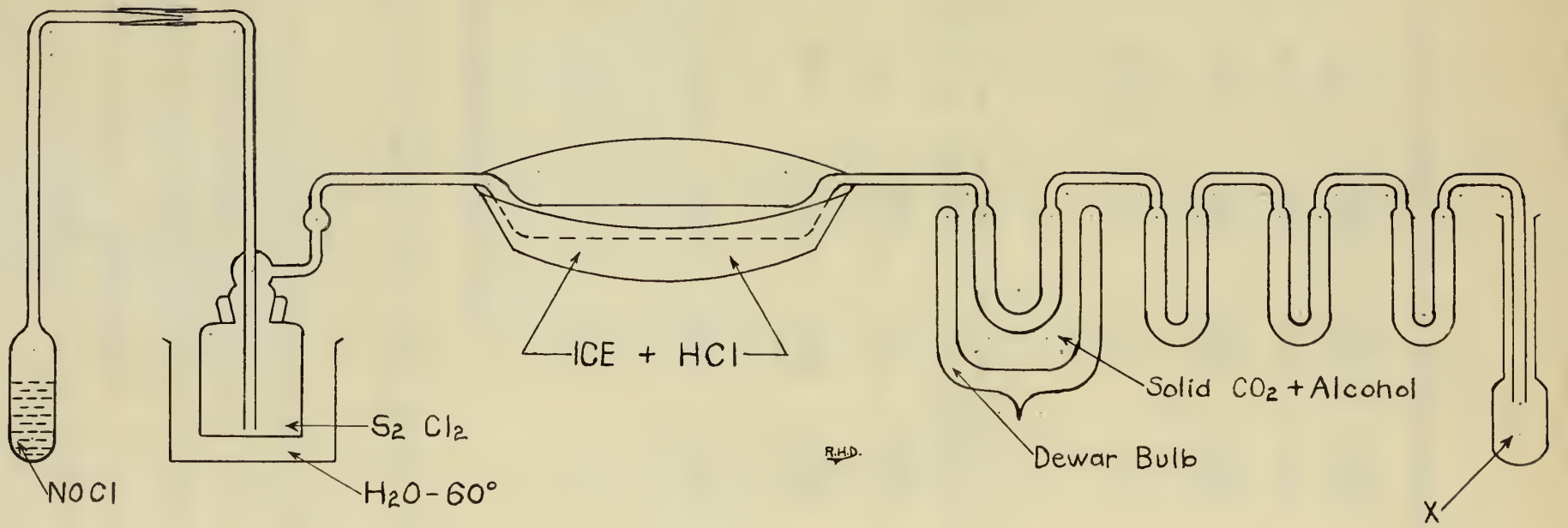
formed.

An experiment was then run by passing separate streams of chlorine gas and nitric oxide, dried by means of concentrated sulphuric acid, through a glass stoppered wash bottle containing S_2Cl_2 surrounded by water kept at 80-90°. This was connected with a porcelain tube about 3/4 inch in diameter, which was heated to redness in a combustion furnace. This in turn was connected to the series of U tubes similar to those shown in Figure 1. The object in this experiment was to have the vapors of S_2Cl_2 carried along with the other two gases into the hot tube, where the reaction would go on. The products obtained were fractionated as usual. The analysis of the product was also carried out as before in the gaseous condition, except that three samples were taken and free sulphur added to two of them to take up any free chlorine which might be present. Here again, the results show no evidence of any nitrogen trichloride having been formed.

Sample No. 1. Most volatile sample.

			Mols	Cl	Acid	Weight
Mols of gas	2.71	NOCl	1.12	1.12	2.24	0.0734
Mols of acid	5.35	SCl_2	0.17	0.34	0.51	0.0175
Atoms of Cl	3.88	Cl_2	1.42	2.84	2.84	0.1008
			2.71	4.30	5.59	0.1917
Atoms of O	0.01					
Atoms of N	1.12	Found	2.71	3.88	5.35	0.1838
Atoms of S	0.178					

FIG. 1



Sample No. 2. Sulphur added before sample was taken.

			Mols	Cl	Acid	Weight
Mols of gas	2.69	NOCl	1.71	1.71	3.42	0.1120
Mols of acid	5.62	Cl_2	0.88	1.76	1.76	0.0625
Atoms of Cl	3.71	SCl_2	0.11	0.22	0.33	0.0113
			2.70	3.69	5.51	0.1858
Atoms of O	0.32					
Atoms of N	1.71	Found	2.68	3.71	5.62	0.1871
Atoms of S	0.11					

Sample No. 3. This was taken from least volatile fraction with an excess of free sulphur present.

			Mols	Cl	Acid	Weight
Mols of gas	2.82	NOCl	2.44	2.44	4.88	0.1586
Mols of acid	5.49	SCl_2	0.30	0.60	0.90	0.0309
			2.74	3.04	5.78	0.1895
Atoms of Cl	2.45					
Atoms of O	0.16	Found	2.82	2.45	5.49	0.1820
Atoms of N	2.44					
Atoms of S	0.298					

Experiments With SCl_2

The SCl_2 was prepared by saturating S_2Cl_2 at 0° with dry chlorine gas.

An experiment was first made with nitrosyl chloride. Some liquid nitrosyl chloride was allowed to evaporate into a glass stoppered wash bottle containing the SCl_2, which was cooled with ice. After the nitrosyl chloride had all evaporated, it was allowed to warm up to room temperature, the gases passing through a long porcelain tube which was gently heated with a moving Bunsen burner.

The gases were collected, fractionated, and analyzed as before, three samples being analyzed.

Sample No. 1. Most volatile fraction.

			Mols	Cl	Acid	Weight
Mols of gas	2.76					
Mols of acid	5.31	NOCl	1.90	1.90	3.80	0.1244
Atoms of Cl	3.35	SCl_2	0.03	0.06	0.09	0.0031
Atoms of O	1.61	Cl_2	0.79	1.56	1.56	0.0561
			2.72	3.54	5.45	0.1836
Atoms of N	1.90					
Atoms of S	0.03	Found	2.76	3.35	5.31	0.1870

Sample No. 2

			Mols	Cl	Acid	Weight
Mols of gas	2.74	NOCl	2.30	2.30	4.60	0.2011
Mols of acid	5.78	SCl_2	0.243	0.49	0.72	0.0504
			2.543	2.79	5.32	0.2515
Atoms of Cl	2.99					
Atoms of O	2.10	Found	2.73	2.99	5.78	0.1888
Atoms of N	2.30					
Atoms of S	0.243					

Sample No. 3. This sample did not completely fill the bulb.

			Mols	Cl	Acid	Weight
Mols of gas	1.51					
Mols of acid	4.59	NOCl	1.23	1.23	2.46	0.0683
Atoms of Cl	2.62	SCl_2	0.37	0.74	1.11	0.0381
			1.60	1.97	3.57	0.1064
Atoms of O	0.65					
Atoms of N	1.23	Found	1.51	2.62	4.59	0.0966
Atoms of S	0.37					

An experiment was then run through with SCl_2 and NOCl with a

slow current of Cl_2 passing through the entire apparatus. The gases were passed through a porcelain tube, heated to redness in a combustion furnace, collected and fractionated as usual.

Sample No. 1. Most volatile sample.

			Mols	Cl	Acid	Weight
Mols of gas	2.698	NOCl	2.22	2.22	4.44	0.1454
Mols of acid	5.53	SCl_2	0.07	0.14	0.21	0.0072
Atoms of Cl	3.17	Cl_2	0.41	0.82	0.82	0.0291
Atoms of O	1.47		2.70	3.18	5.47	0.1817
Atoms of S	0.07	Found	2.70	3.17	5.53	0.1805
Atoms of N	2.22					

Sample No. 2.

			Mols	Cl	Acid	Weight
Mols of gas	2.75	NOCl	2.73	2.73	5.46	0.1788
Mols of acid	5.95	SCl_2	0.14	0.28	0.48	0.0144
Atoms of Cl	2.93		2.87	3.01	5.94	0.1932
Atoms of O	2.06	Found	2.75	2.93	5.95	0.1881
Atoms of N	2.73					
Atoms of S	0.147					

Sample No. 3. This was allowed to evaporate into a normal solution of NaOH

Mols of acid	21.868	Weight of Cl	0.4566
Atoms of O	3.45	Weight of S	0.0270
Atoms of S	0.844	Weight of N	0.0287
Atoms of Cl	12.864	Weight of O	0.2450
			0.7673

Weight of liquified gas by difference 0.7573. The gas was not all absorbed.

All of the experiments with the chlorides of sulphur failed to give any evidence of any nitrogen trichloride having been formed.

An experiment was then run with hydrochloric acid and NO gas, but with negative results.

NO was passed through concentrated HCl heated to 60°, thus making the gas 25% HCl. The gases were dried with H_2SO_4 and then passed over PCl_5, heated to 105-110° in an oil bath. The gases were then collected as usual with solid CO_2 and alcohol, and fractionated. The NO which would not condense was collected and measured. About 10 liters of NO were used and 7 liters of gas were collected during the experiment.

			Mols	Cl	Acid	Weight
Mols of gas	2.61	NOCl	2.61	2.61	5.22	0.1710
Mols of acid	5.64	Found	2.61	2.76	5.64	0.1766
Atoms of Cl	2.76					
Atoms of O	1.93					

Assuming the gas was pure NOCl, the following figures would result:

This cannot be so, for the calculated value for the atoms of N on this basis is 2.88, which is too great. I suspect the presence of some HCl in the gas which will make up the difference in the values of the Cl and acid.

The analysis of the products obtained from $AsCl_3$ and (NOCl ?), which had been sealed up for some time, resulted as follows:

			Mols	Cl	Acid
Mols of gas	2.73	NOCl	2.67	2.67	5.34
Mols of acid	5.49	NCl_3	0.06	0.18	0.72
Atoms of Cl	2.82			2.85	6.06
Atoms of O	1.88	Found		2.85	5.49
Atoms of N	2.67				

Attempts To Obtain Direct Combination of Chlorine and Nitrogen

An attempt was then made to secure the nitrogen trichloride by combining the elements of chlorine and nitrogen under the influence of the electric arc. It has long been known that under the influence of the electric arc, nitrogen and oxygen combine quite readily and this process has been put on a commercial basis for the production of nitrates and ammonia.

The high temperature produced in the arc together with the different electrical effects produced by the discharge, would tend to set the molecules of the two gases vibrating much more rapidly. Under these conditions collision of the molecules would occur more frequently and with greater violence, thus tending to cause them to split apart into atoms and also to ionize.

Mixtures of chlorine and nitrogen free from oxygen were allowed to pass through an arc formed between platinum electrodes. The arc was produced by an induction coil which was made by the Thordarson Electric Mfg. Co. of Chicago, and is rated at 20,000 volts. The arc was spread by placing the bulb which contained the electrodes between the armatures of a powerful electro-magnet, through which a current of 20 amperes was passed. The magnet was wound with about 75 yards of No. 10 wire in four layers.

Atmospheric nitrogen was used in these experiments. The oxygen was removed from the air by means of the apparatus designed by Van Brunt[1]. The nitrogen delivered by this apparatus was further purified by passing it over copper foil heated in an electric furnace to dull redness, so as to absorb any trace of oxygen not re-

1 J. Am. Chem. Soc. 36, 1448 (1914)

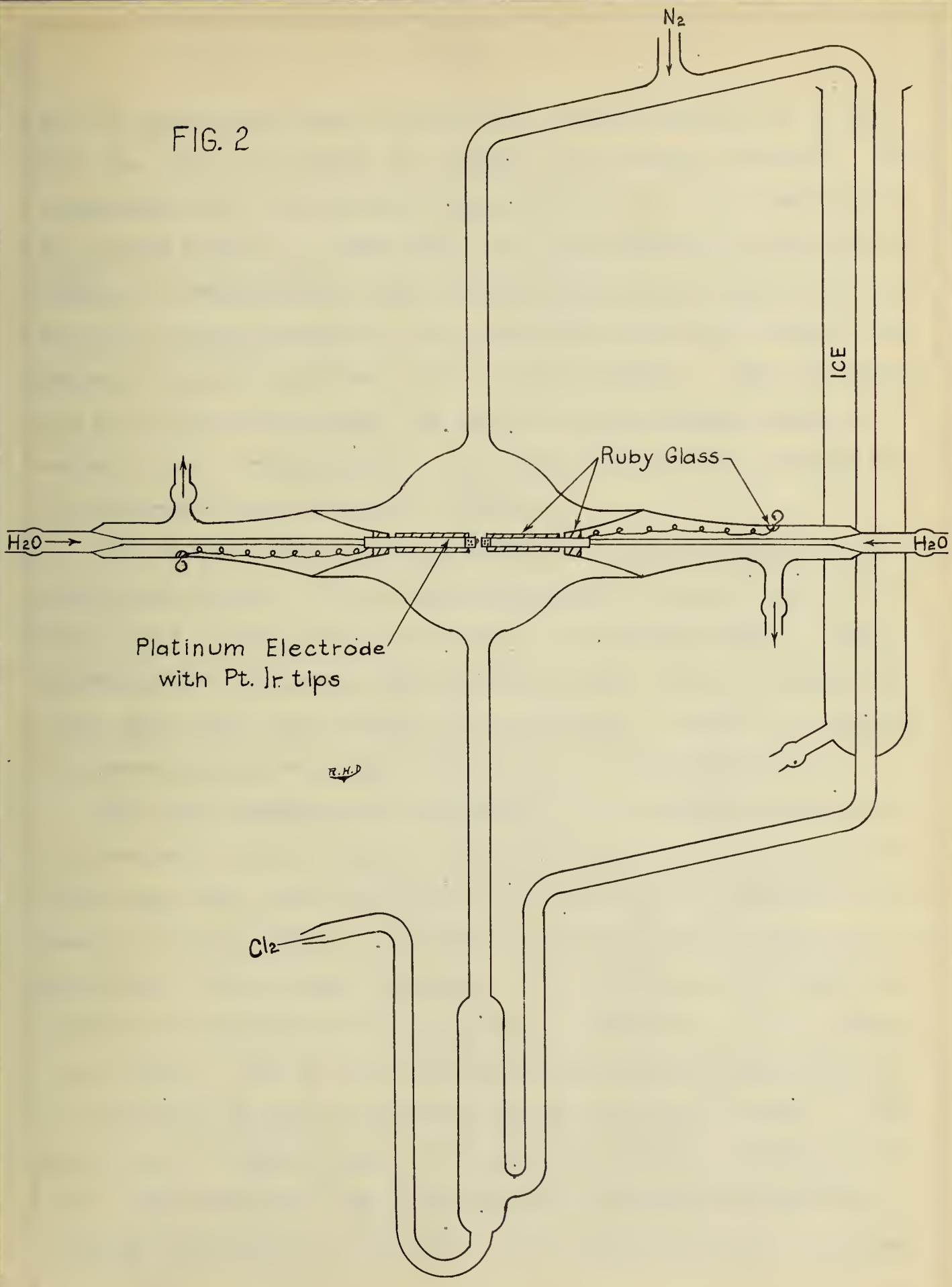
moved before. The gas was then washed with dilute sulphuric acid to remove ammonia, twice with concentrated sulphuric acid, and it was finally dried by means of phosphorus pentoxide.

Chlorine was generated in an all glass apparatus. Chemically pure hydrochloric acid was added to pure manganese dioxide in a flask which was heated on a water bath. The chlorine was washed with water, 1 : 1 sulphuric acid, concentrated sulphuric acid and finally dried with phosphorus pentoxide.

The apparatus, Figure 2, consists of hollow platinum electrodes covered with a thin coating of soft glass to protect them from the action of the chlorine, sealed into a bulb with their ends about 1 mm. apart. The electrodes were connected with a water cooling device, distilled water being used. Sealed into the bottom of the bulb is a reservoir for collecting chlorine. This is fitted with an outlet to be sealed on to the chlorine generator and also connects with the outlet coming from the top of the bulb for connection with the nitrogen generator. The jacket, surrounding the tube on one side and connecting the top and bottom of the apparatus, is filled with ice, which will cause a current to be set up within the apparatus, thus causing the gases to flow continually through the arc.

Method of Operation. The apparatus was sealed to the nitrogen generator at the top through a three way stopcock, and to the chlorine generator at the bottom. By means of the three way stopcock the apparatus was evacuated by means of a water pump, and then filled with nitrogen. This was repeated several times after which about 5 cc. of liquid chlorine was condensed in the reservoir of CO_2 snow. The outlet to the chlorine generator was then sealed off,

FIG. 2


N_2
ICE
Ruby Glass
H_2O
H_2O
Platinum Electrode
with Pt. Ir tips
R.H.D
Cl_2

the CO_2 snow removed and the chlorine allowed to nearly all evaporate, the gases being swept out through the three-way stopcock. This evaporation will boil out any oxygen which may be held dissolved in the liquid chlorine. When only two or three drops of liquid chlorine remain, the apparatus is again connected with the nitrogen generator, the CO_2 snow again applied to the reservoir and as the chlorine condenses the apparatus becomes filled with nitrogen. When the apparatus is filled with nitrogen the outlet to the nitrogen generator is sealed off. The apparatus is then placed between the poles of the electro-magnet and the current turned on.

The arc was about 18 cm. in diameter. The runs usually lasted about three hours. It was found advantageous to leave the current on for half an hour and then turn it off for five mintues. This prevented the electrodes from becoming so hot, thus preventing the glass where they were sealed in from cracking. During the sparking the reservoir at the bottom was immersed in a freezing mixture.

When the sparking had been completed, CO_2 snow was applied to the reservoir, which condensed the excess chlorine and any product which might have formed and gave a pressure equal to atmospheric pressure within the bulb. It was then opened at the top first and connected with the nitrogen generator. The chlorine outlet was then opened and connected with a spiral which contained 1 cc. of conductivity water. The CO_2 snow was then removed slowly enough so that the condensed chlorine evaporated through the spiral slowly. The apparatus was finally swept out through the spiral by means of nitrogen. The spiral was then washed out with conductivity water, the washings being made up to 15 cc. In this way any gaseous compound

of nitrogen would be hydrolyxed according to the reaction

$$NCl_3 + 3H_2O + Cl_2 = HNO_3 + 5HCl$$

5 cc. of this solution was analyzed for us by the Illinois State Water Survey for nitrates by reducing the solution with aluminium for 12 hours and then distilling the ammonia and determining it by Nessler's solution. The chlorine was determined by Volhard's method of precipitating the chlorine with an excess of standard silver nitrate and titrating the excess with ammonium thiocyanate.

Results. A great deal of difficulty was encoutnered in working with this apparatus because of the glass cracking where the electrodes were sealed in, and also because the electrodes were attacked to such an extent by the chlorine that they were eaten through. In each case water would be admitted to the apparatus, thus introducing oxygen, which spoiled the results. The latter difficulty was overcome somewhat by filling the ends of the electrode with gold and covering the outside of the electrodes with a thin coat of soft glass.

The results obtained were as follows:

	Mg N	Mg Cl	Mg at Cl	Mg at N
1.	0.156	11.92	0.336	0.011
2.	0.148	17.93	0.500	0.0105
3.	0.024	35.14	0.990	0.002
4.	0.768	11.50	0.324	0.055

In experiment No. 4 one electrode was eaten through by the chlorine before completion, thus accounting for the higher value for the nitrogen. Otherwise it is seen that practically no gaseous compounds of nitrogen were obtained, showing that under the influence of the electric arc practically no reaction takes place between chlorine and nitrogen.

Reaction Between Anhydrous Chlorine And Ammonia

Attention was next turned to the reaction between chlorine and ammonia. In 1901, Noyes and Lyons[1] demonstrated that nitrogen trichloride and free nitrogen are formed in equimolecular quantities when chlorine gas is treated with 0.5% NH_3 solution in proportion of 1 mol Cl_2 to 1.90-1.95 mols NH_3. They give the following equation

$$3NH_3 + 6Cl_2 = N_2 + NCl_3 + 9H^+ + 9Cl^-$$

and they state that 6 mols of chlorine must react simultaneously with 3 mols of ammonia. Later Bray and Dowell[2] made a study of this reaction in which these substances were mixed in the proportion of 1 mol of Cl_2 to 2 mols of NH_3. They found a series of rapid reactions taking place which varies, depending on the conditions of the reaction mixture.

Thus they found that nitrogen trichloride is formed very rapidly and almost quantitatively when strong acid is present, according to the following reactions.

$$NH_3 + 3Cl_2 = NCl_3 + 3H^+ + 3Cl^-$$

$$NH_4^+ + Cl^- + 3Cl_2 = NCl_3 + 4H^+ + 4Cl^-$$

$$NH_4^+ + Cl^- + 3HClO = NCl_3 + H^+ + Cl^- + 3H_2O$$

If the solution becomes alkaline, nitrogen gas is evolved rapidly and almost quantitatively as expressed in the following equations.

$$2NH_3 + 3Cl_2 = N_2 + 6H + 6Cl^-$$

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4 + 6Cl^-$$

$$2NH_3 + 3ClO^- = N_2 + 3Cl^- + 3H_2O$$

These authors improved the mthods of obtaining and analyzing NCl_3

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1 J. Am. Chem. Soc 23, 460 (1901)
2 J. Am. Chem. Soc 39, 908 (1917)

as given by Hentschel[1] and Bineau,[2] in which the trichloride was extracted with carbon tetrachloride and reduced with a saturated sodium sulphite solution.

It was, therefore, proposed to study the reaction in an anhydrous environment, using carbon tetrachloride as a solvent. Although the nitrogen in ammonia is positive, the hypothesis proposed by Noyes and Lyons[3] was taken as a working basis, in which they make the supposition that all reactions involving the decomposition of molecules are preceeded by an ionization of the parts of those molecules, whether the molecules be made up of two atoms of the same element or of different elements. If this be true the nitrogen atom might be present in both the positive and negative form, as well as the chlorine atom being present in both the positive and negative form. In this way the nitro nitrogen trichloride could be formed as well as the ammonia nitrogen trichloride. These products would be dissolved in the carbon tetrachloride and could then be analyzed.

Experimental part. The reactions were carried out at low temperatures for various reasons. 1. The reaction between dry chlorine and dry ammonia is very vigorous and generates much heat. 2. The reduction of temperature would reduce the probability of the products being decomposed by the heat generated in the reaction. 3. The substances both being gases, become liquified and are easily handled.

The temperature worked at was -70 to -80°, secured by means of solid carbon dioxide and alcohol made into a mush. The chlorine was prepared by droping pure hydrochloric acid on potassium permanganate. The gas was purified by washing it with water and dried by passing it

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1 Ber. 30, 1792 (1897)
2 Ann. Chim. Phys. (3) 15, 71 (1845)
3 J. Am. Chem. Soc. 23, 460 (1901)

through two wash bottles of concentrated sulphuric acid. It was then passed into a small bulb of about 10-15 cc. capacity, surrounded with solid CO_2, thus liquifying the gas. It was then sealed up for future use.

Ammonia was prepared by gently heating an ammonium hydroxide solution of specific gravity 0.9. It was passed through a U-tube surrounded by ice to condense any excess of water and was dried by passing it over soda lime, and finally over solid caustic potash. The dry gas was then passed into a bulb and liquified and sealed as in the case of the chlorine.

Small bulbs capable of holding as much as three grams of the liquids were blown on one end of a piece of heavy capillary tubing. The other end was drawn out to a fine capillary long enough to reach to the bottom of the bulbs containing the liquified gases. The tubing was bent so it could be handled conveniently, then by warming the bulb, with the capillary end dipping beneath the surface of the liquified gas, some of the air is forced out. Now by cooling the bulb with solid CO_2, the air will contract, drawing some of the liquified gas into the bulb. It may become a gas in passing up the tube, but will liquify after coming into the bulb. After a small quantity of liquid has condensed in the bulb, the CO_2 is removed and the gas allowed to evaporate thus driving out all the air. The bulb is again surrounded by the solid CO_2 and as much liquid condensed as is desired. The capillary tube is then sealed off. By weighing the bulb before and after filling, the quantity of material is known.

In carrying out an experiment the bulb is first weighed, then cooled with CO_2. The capillary tube is broken off and the bulb still

surrounded with CO_2 is attached to the apparatus in which the reaction is to be carried out. The CO_2 is then removed and the gas allowed to evaporate into the apparatus, which had previously been exhausted. When the liquid gas has all evaporated the bulb is disconnected and reweighed, the loss in weight giving the amount of gas used.

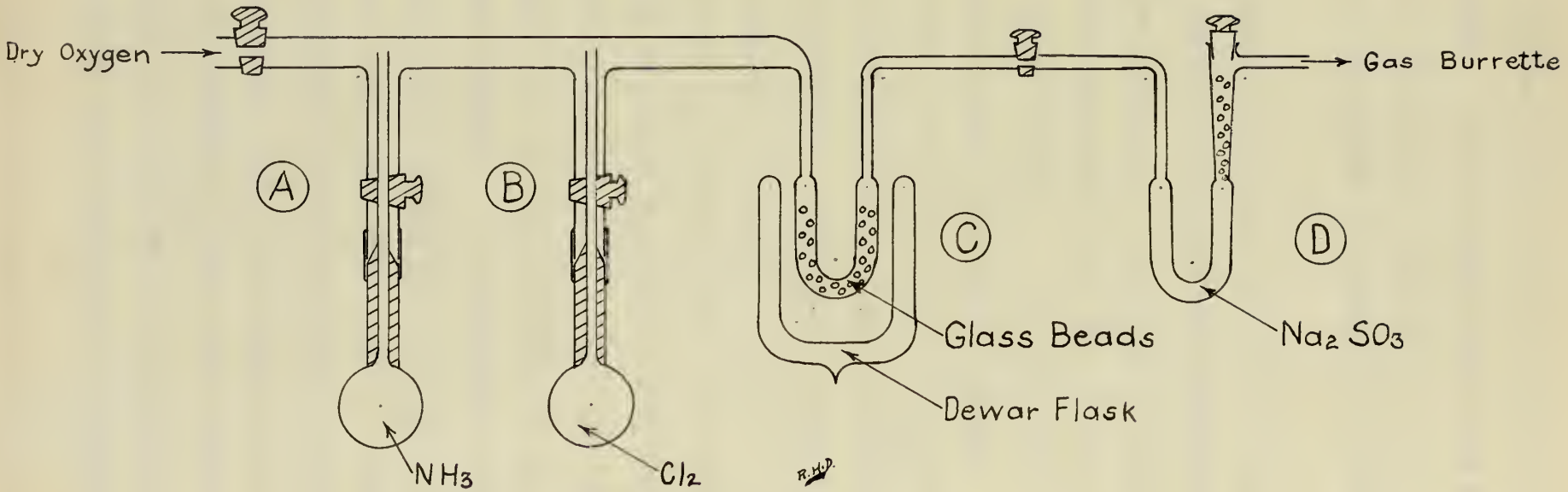
The first experiments were carried out in a bulb having a capacity of about 100 cc., which was fitted with a three-way stopcock. About 25 cc. of carbon tetrachloride was introduced into the bulb. The bulb of chlorine was connected at one outlet of the stopcock by means of a rubber joint, care being taken to bring the glass tubing close together. The other outlet of the stopcock was connected with a water pump and the bulb exhausted till the carbon tetrachloride boiled. The bulb was then placed in a Dewar flask and surrounded with solid CO_2. The CO_2 around the small bulb containing the liquid chlorine was then removed, thus allowing the chlorine to evaporate into the large bulb where it would be dissolved in the carbon tetrachloride, as well as being liquified. When it had all evaporated, the stopcock was closed, the chlorine bulb removed and the ammonia bulb put in its place, and the ammonia allowed to evaporate into the bulb.

When this was completed, the large bulb was connected to a similar bulb which had been well exhausted. It was cooled with CO_2, while the other bulb was allowed to warm up to room temperature. In this way the carbon tetrachloride and the products dissolved in it distilled into the other bulb, leaving the solid ammonium chloride which was formed during the reaction. The bulb was finally heated to about

70° to drive out the last traces of carbon tetrachloride.

The ammonium chloride was determined in some cases by weighing the bulb before starting and after the experiment was finished, and in others by dissolving the material left in the bulb and determining the ammonia and chlorine in this solution. The distillate in the other bulb was shaken with sodium sulphite solution. The carbon tetrachloride was separated and washed twice with distilled water and the combined aqueous solution made up to 100 cc. The ammonia and chlorine were then determined. In all these experiments the ammonia was determined by distilling into standard acid from a strongly alkaline solution, and the chlorine was weighed as silver chloride in the earlier experiments, and titrated according to Volhard's method in the later experiments. This method of procedure had the disadvantage of not offering a large enough space. Small quantities of liquid gas had to be used. They did not always go in readily, losses occuring in some of the experiments. This was due largely to the free nitrogen which was formed during the reaction. In order to overcome the difficulties and to measure the amount of nitrogen formed more accurately a second apparatus was designed. A drawing of this apparatus is shown in Figure 3. The apparatus was constructed entirely of glass. The apparatus consisted of two stopcocks A and B, through which the gases were introduced. These were sealed on to a U-tube containing glass beads which was the place in which the reaction was carried out. It was, therefore, placed in a Dewar bulb for cooling. The object of the beads was to collect the chlorine which was introduced as it condensed, thus distributing it. This allowed the reaction with the ammonia when it was introduced to proceed more slow-

FIG. 3


Dry Oxygen
A
B
C
D
Gas Burrette
Glass Beads
Na2 SO3
Dewar Flask
NH3
Cl2

ly, and also prevented the ammonium chloride which was formed from stopping up the apparatus. In this form runs were made without any solvent, after which the beads were removed and three different solvents used, chloroform, experiment 6-8, pentane, experiment 9-10 and carbon tetrachloride.

Sealed to the reaction U-tube was another U-tube containing sodium sulfite of known strength to absorb any gaseous compounds of nitrogen formed during the reaction. A column of beads was sealed to this apparatus over which the sodium sulfite was run in to insure a more efficient scrubbing of the gas. The experiment was carried out as follows. The apparatus was filled with oxygen. While a slow stream of oxygen continued to flow through the apparatus, a known volume of sodium sulfite was added to D and the bulbs of liquified gases were connected at A and B. The carbon dioxide was removed from the chlorine bulb and the liquid was allowed to evaporate into C, the stopcocks beyond being open to permit the escape of oxygen displaced. The ammonia was then allowed to evaporate into C, the stopcock between C and D being closed. When this was completed, the current of dry oxygen was started through the apparatus and the gases collected in a gas burette. The oxygen of the collected gas was absorbed with pyrogallol in a Hempel pipette, the residue being nitrogen. The apparatus was then taken apart. The sodium sulfite was titrated with permanganate and its chlorine and ammonia contents determined. The solvent in C was distilled out as in the case of the bulb of the first experiments, shaken with sodium sulfite and the aqueous solution made up to 100 cc; after which the chlorine, ammonia and oxidizing power were determined. The ammonium chloride

remaining in the apparatus was dissolved in distilled water and the chlorine and ammonia determined.

In experiments 8 and 9 liquid air was used in order to secure a lower temperature. This necessitated the use of other solvents as carbon tetrachloride freezes at -19°. Chloroform in experiment 8 and pentane in experiment 9 were used, but this change did not yield any marked advantage. The freezing of the solvents by the liquid air made it possible for the reaction to go on more slowly as the solvents slowly melted.

The results with this apparatus were much better than in the case of the single bulb, but even here the lack of control was evident, so a third apparatus was tried, really an enlargement on the first plan. The apparatus consisted simply of a hard glass bomb tube about 40 cm. long and 2 cm. in diameter. The top was drawn out according to this drawing and a stopcock attached.

The experiments with these tubes were run as follows. The tubes were exhausted below 10 mm. by an oil pump. They were then placed in a long Dewar flask and surrounded with solid carbon dioxide. An ammonia bulb was then connected at A, the stopcock opened and the ammonia allowed to distill into the tube. The stopcock was then closed and a bulb of 25-30 cc. capacity filled with carbon tetrachloride was connected at A, and while the tube was inclined at an angle of 15° by opening the stopcock the carbon tetrachloride was allowed to enter the tube. In this way the carbon tetrachloride with the liquid ammonia distributed through it is frozen along the side of the tube. The bulb of liquid chlorine was now attached and the chlorine

allowed to evaporate into the tube. When the chlorine had all evaporated, the tube was sealed at B, the constriction being made to facilitate sealing the partially evacuated tube. The tube was then placed in a horizontal position and left over night, during which time it warms up slowly and the reaction takes place slowly.

In a few of the earlier experiments the tube was placed in a perpendicular position and the carbon tetrachloride frozen on top of the ammonia, and then the chlorine coming in on top of the carbon tetrachloride. It was found under this arrangement that the gases had not thoroughly mixed, the ammonia evidently not diffusing up through the carbon tetrachloride, for on mixing the solution in the morning further reaction took place with evolution of considerable heat.

In the morning, if a rough estimate of the amount of nitrogen evolved was secured, the tube was cooled to 0°, rubber connections were wired on at C, which connected with a gas burette set at 50 cc., the tip at B was then broken and the amount of gas entering the tube or entering the burette was noted. Knowing the volume of the tube above the carbon tetrachloride solution, the vapor pressure of carbon tetrachloride at 0°, and the volume of gas at the end of the experiment, a rough estimate of the amount of nitrogen formed was arrived at.

The tube was then opened at C, the carbon tetrachloride solution was filtered through a Gooch funnel into a solution of sodium sulfite of known strength. The tube and ammonium chloride in the funnel were washed several times with dry carbon tetrachloride. The sodium sulfite solution was separated from the carbon tetrachloride, made up to 100 cc. and its oxidizing power and chlorine and ammonia contents

determined. The ammonium chloride remaining in the tube and on the funnel was dissolved in water and chlorine and ammonia determinations made on it.

Table I

Expt Number	Atoms Cl	Mols NH_3	Mols NH_4Cl	NH_4Cl cal. as 3/4 NH_3	Mols NCl_3	Atoms N	Mols Nitrite	Solvent
1	18.60	12.40	9.20	9.30	1.05	3.92		CCl_4
2	103.40	67.99	18.85	50.97	2.32			CCl_4
3	28.36	25.20	25.57	18.90	8.90			CCl_4
4	39.22	25.56	20.40	19.17	8.94			CCl_4
5	48.98	22.75	18.67	17.07				CCl_4
6	26.93	11.81	6.29	8.85	8.70			$CHCl_3$
7	33.96	19.30	14.05	14.46	1.96	2.91		$CHCl_3$
8	30.30	19.87	14.70	14.91	.66	4.70		$CHCl_3$
9	20.00	10.00	6.19	7.50	3.90	2.54		Pentane
10	42.03	28.35	20.50	21.27	1.75	5.93		Pentane
11	44.22	27.17	16.46	20.37	1.63	6.26		None
12	53.98	36.00	26.94	27.00	3.00	8.20		CCl_4
13	62.22	46.44	34.75	34.83	0.89		0.15	CCl_4
14	75.03	45.51	33.94	34.17	0.80	9.40	0.12	CCl_4
15	58.73	44.90	33.55	33.60	0.046	10.11	0.10	CCl_4
16	80.63	66.16	49.42	49.62	0.22		0.11	None
17	87.62	54.70	40.82	41.03	0.46		0.11	None
18	83.62	36.48	26.67	27.36	1.51		0.16	CCl_4
19	45.64	55.53	41.54	41.65	1.05		0.38	CCl_4

Table II

Expt Number	Atoms Cl	Mols NH_3	Mols NH_4Cl	Mols NCl_3	Atoms N	Mols Nitrite	Solvent
1	6.00	4	2.97	0.338	1.27		CCl_4
2	6.08	4	1.11	0.137			CCl_4
3	3.71	4	4.06	0.141			CCl_4
4	6.14	4	3.19	0.134			CCl_4
5	8.61	4	3.28				CCl_4
6	9.12	4	2.13	0.294			$CHCl_3$
7	7.04	4	2.97	0.406	0.603		$CHCl_3$
8	6.10	4	2.96	0.132	0.946		$CHCl_3$
9	8.00	4	2.48	0.156	1.016		Pentane
10	5.99	4	3.04	0.246	0.837		Pentane
11	6.51	4	2.42	0.240	0.925		None
12	6.00	4	2.99	0.333	0.911		CCl_4
13	5.36	4	2.99	0.077		0.012	CCl_4
14	6.59	4	2.98	0.070	0.826	0.015	CCl_4
15	5.23	4	2.98	0.004	0.901	0.004	CCl_4
16	4.88	4	2.99	0.013		0.003	None
17	6.36	4	2.98	0.034		0.008	None
18	10.54	4	2.92	0.165		0.017	CCl_4
19	3.28	4	2.99	0.075		0.027	CCl_4

Discussion of Results

Evidence of the formation of any nitro nitrogen trichloride was practically negative. In experiments 13 to 19, after the ammonia was distilled from the sodium sulfite solution, the residue was diluted up with distilled water and the solution reduced with Divarda's alloy. Thus any nitrate present would be reduced to ammonia and this was distilled. Indications were obtained of some of the compound being present, but only in very small amounts. Interesting results, however, were obtained which throw some light on the mechanism of the reaction of chlorine and ammonia. Experiments 1 to 6 do not show such good results as the others. These experiments were carried out in the small bulb and the high results obtained for the ammonium chloride in experiments 3, 4, and 5 are due probably to the fact that the ammonium chloride contained some of the solvent which had not been completely removed. In experiments 2, 6 and 11, ammonia was lost during the evaporation from the small bulb, giving low results.

In all the other experiments it is seen that three-fourths of the ammonia taking part in the reaction is converted into ammonium chloride, according to the reaction

$$3Cl_2 + 4NH_3 = 3NH_4Cl + NCl_3$$

This striking result is obtained regardless of whether an excess of either chlorine or ammonia was used over the amount necessary for the above reaction. This fact is brought out more sharply in Table II, in which the ammonia is recalculated so that it becomes 4 and the other values of the products reduced proportionally to this basis. Thus, according to the reaction, 4 mols of ammonia required 6 atoms

of chlorine to react with it, producing 3 mols of ammonium chloride and 1 mol of nitrogen trichloride. In experiments 1, 4 and 12, the exact ratio was obtained and in each case 3 mols of ammonium chloride were produced. In experiments 7, 8, 9, 14, 17 and 18, the value for the atoms of chlorine used are greater than six, so an excess of chlorine was present, but the ammonium chloride value remains constant at 3. In experiments 13, 15, 16 and 19, it is seen that there was an excess of ammonia present, but the ammonium chloride continues to remain constant. If we look at the values for the nitrogen trichloride in the product we find that they are very low in all cases. None of them approach 1, the value expected. From this it is concluded that under the conditions of these experiments, nitrogen trichloride decomposes almost entirely into free chlorine and nitrogen. This fact will explain why the ammonium chloride value remains constant when less than the theoretical amount of chlorine is used to react with the ammonia, since the decomposition of the nitrogen trichloride gives chlorine to make up the deficiency. It is also possible that the nitrogen trichloride will react with the ammonia direct as follows

$$NCl_3 + 4NH_3 \longrightarrow 3NH_4Cl + N_2$$

Here the relation between the ammonia and ammonium chloride is still 4 to 3, with one mol of nitrogen produced.

Also, by adding this equation and the one on Page 22 we have

$$3Cl_2 + 4NH_3 \longrightarrow 3NH_4Cl + NCl_3 \qquad (1)$$

$$NCl_3 + 4NH_3 \longrightarrow 3NH_4Cl + N_2 \qquad (2)$$

$$3Cl_2 + 8NH_3 \longrightarrow 6NH_4Cl + N_2 \qquad (3)$$

To test out this reaction experiment 19 was run with a very

great excess of ammonia. 0.9441 gram of NH_3 was taken. To react with this, according to reaction (1), 2.9572 grams of chlorine would be required. To react, according to (3), 1.4786 grams of chlorine would be required. 1.6193 grams was actually used. It is seen that there was quite an excess of chlorine used for reaction (3), which explains the comparative large yield of nitrogen trichloride.

In experiments 7 to 15 (excluding 13), in which nitrogen was determined, it was found that the sum of the values for the nitrogen and the nitrogen trichloride is as near one as can be expected, considering the approximate determination made for the nitrogen. In experiment 16 and 17 the reaction was run without any solvent without producing any change in the results. It is noticed, as would be expected, that more nitrogen trichloride is obtained in No. 17, in which an excess of chlorine was used, while an excess of ammonia was used in No. 16. Unfortunately the nitrogen in these experiments was lost. In experiment 18, in which a very large excess of chlorine was used, it is seen that the amount of ammonium chloride produced falls a little, while the amount of nitrogen trichloride is higher than in any of the experiments from 13 to 19. It is probable that with such a large excess of chlorine present some of the ammonium chloride was attacked, producing nitrogen trichloride.

These experiments seem to point to the fact that nitrogen trichloride is formed by a direct reaction of the chlorine and ammonia.

The reaction is probably not a tenth order reaction as shown in (1), but takes place in steps, NH_2Cl being the primary step, this compound having been isolated by Raschig[1].

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1 Chem. Ztg. 31, 926 (1907)

Attempts To Prepare A Phosphoro Phosphorus Trichloride

Most of the experiments with PH_3 led to negative results, but the preliminary experiments we made with PH_3, HOCl and NaOCl might be investigated further. These were two in number and were carried out as follows.

A water solution of HOCl was distilled from bleaching powder in acid solution and a little of this solution admitted to an evacuated bulb with a little benzene. PH_3 was then admitted and the bulb well shaken. The solutions were then removed from the bulb, separated in a separatory funnel and the benzene solution shaken with As_2O_3. This As_2O_3 solution was separated from the benzene and tested, qualitatively for P and Cl. Positive tests were obtained, while negative tests were obtained when the experiment was carried out without introducing any PH_3. The above experiment was repeated with a solution of NaOCl and similar results obtained.

Summary

Reactions with S_2Cl_2, SCl_2, $AsCl_3$ and PCl with NOCl or Cl_2 failed to yield any compound containing positive nitrogen. Dry chlorine and dry nitrogen do not unite under the influence of the electric arc. The reaction between dry chlorine and dry ammonia either alone or in the presence of anhydrous solvents proceeds in such a course that three-fourths of the ammonia entering the reactions is converted into ammonium chloride with the production of nitrogen trichloride, which either decomposes into chlorine and nitrogen if an excess of chlorine is present, or reacts with any excess ammonia, yielding free nitrogen. In every case the ratio between the ammonia and ammonium chloride is 4 to 3.

Evidence of positive nitrogen compounds being formed in the reaction was only slight.

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Gaylord
PAMPHLET BINDER
Syracuse, N. Y.
Stockton, Calif.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 079097421